PFAS IN THE ENVIRONMENT

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ENVIRONMENTAL SHOW OF THE SOUTH

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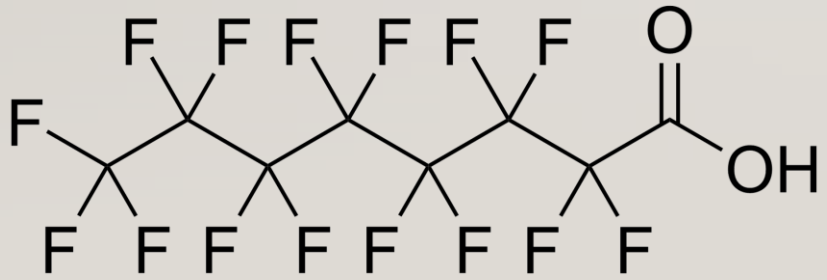
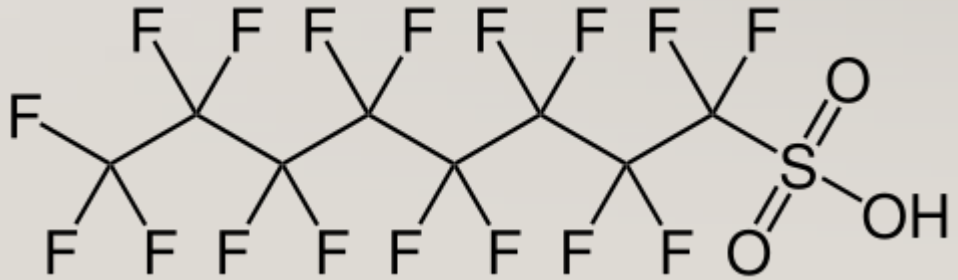
PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

- Umbrella term
- "PFC" no longer used
- Aliphatic carbon chain -- no aromatic rings, no chlorofluorocarbons (refrigerants)
- PFAS are family of more than 5,000 manmade chemicals

PFOA or "C8"

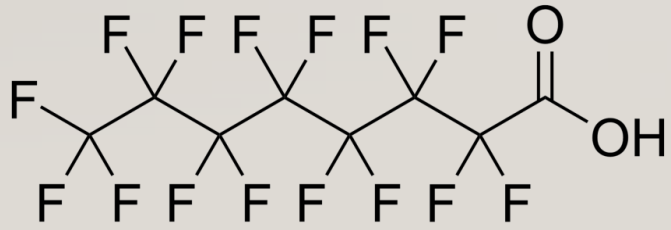


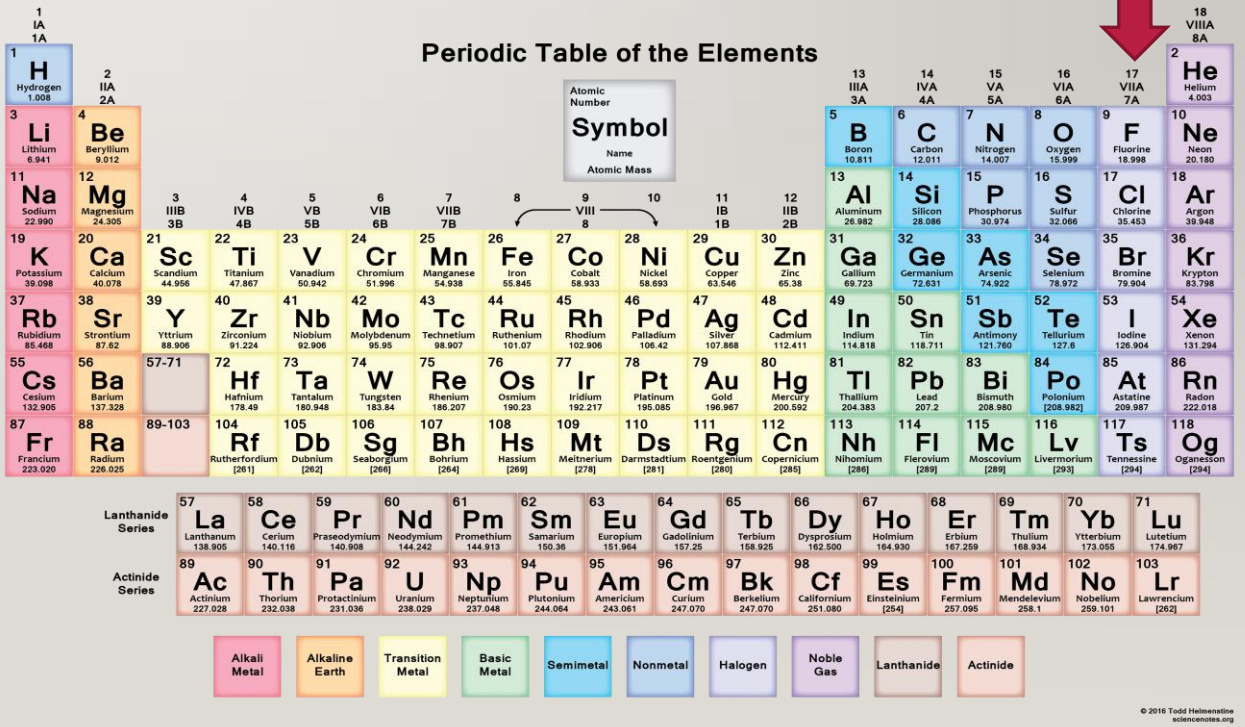
PFOS



WHAT'S SO SPECIAL ABOUT PFAS?

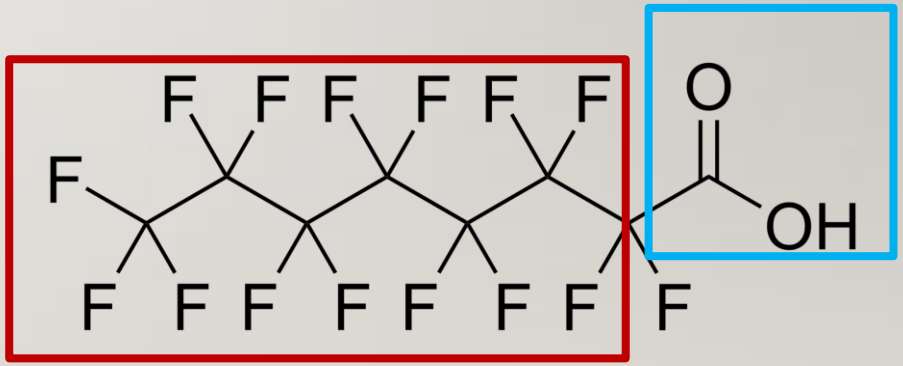
- Carbon – Fluorine bond is SO STRONG
  - Short bond length (electronegativity of F)
  - Need higher energy to break bond
- Low polarizability of F
- Small size of F
  - Shields carbon



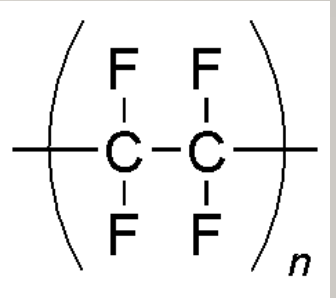


UNIQUE PROPERTIES OF PFAS

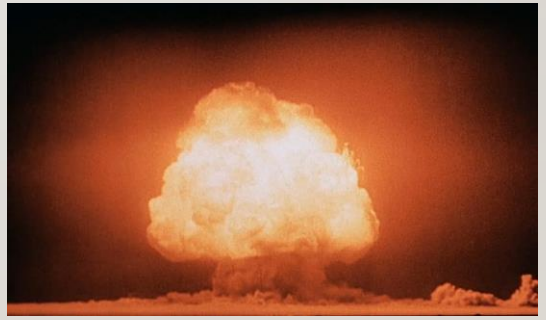
- Thermal stability
- Chemical stability
- When paired with polar functional group
  - Both hydrophobic and lipophobic (surfactant properties)
  - When functional group is acidic – strong acid
- Many unique applications in products – unfortunately also some unique environmental challenges



HISTORY



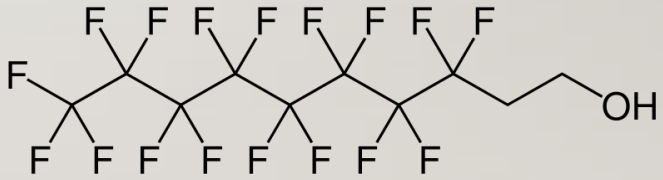
- In 1938, DuPont scientist accidentally discovered polytetrafluoroethylene (PTFE - Teflon)
- DuPont did not find a use for it at the time
- Manhattan Project – 1939-1946
  - Enrichment of U^{235} using gaseous UF_6 (corrosive)
  - Needed highly resistant coolants and solvents
  - DuPont scientists recall PTFE properties
  - Liquid fluorocarbons are used for the first time



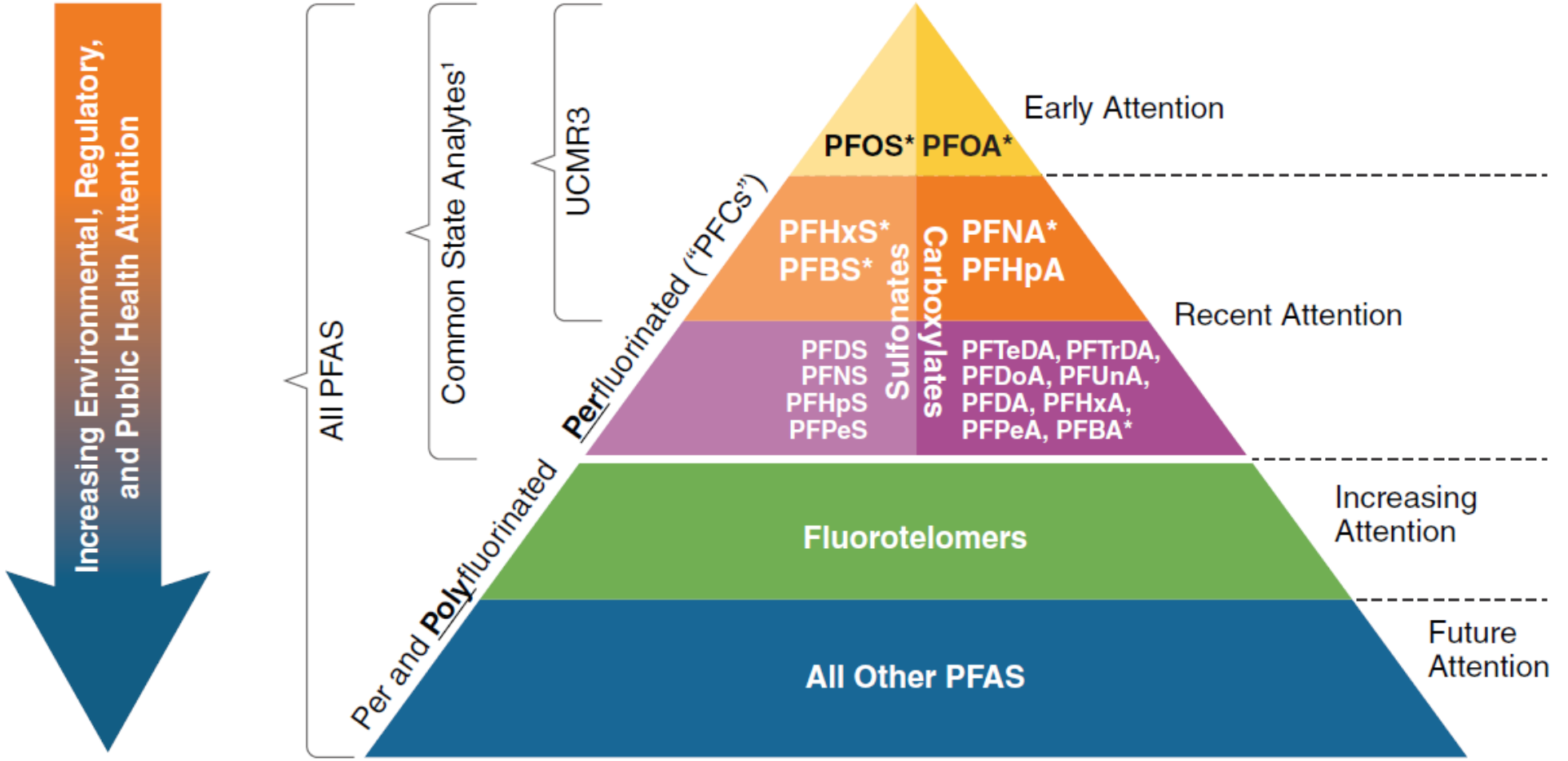
- After the war, technology was declassified and commercialization begins in 1949

PRODUCTION

- Electrochemical Fluorination (ECF) – one of the declassified methods for producing fluorinated alkanes
  - Hydrocarbon + HF + e^- → Fluorocarbon
  - 3M licensed ECF technology from Simons (Penn State)
  - Messy synthesis – many impurities (straight and branched chains)
- Telemerization process
  - Building by blocks of "2"
  - 8:2 FTOH
  - Precursor compounds degrade in the environment to more stable perfluorinated compounds



- Hexafluoropropylene Oxide (HFPO) chemistry
  - Readily reacts with nucleophiles
  - Building block for many fluorochemicals (GenX)



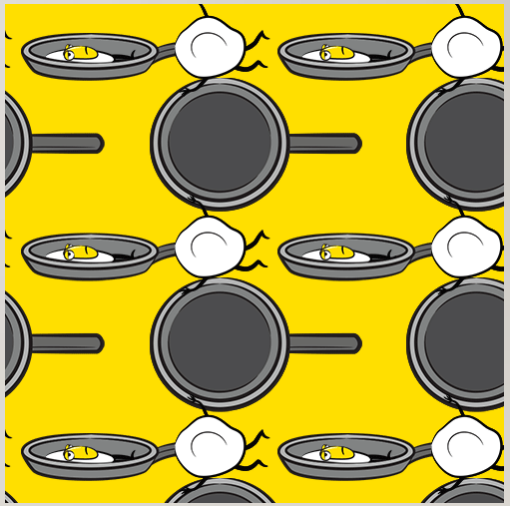
*Common regulatory criteria or health advisories
[1]Sum of informal poll (NJ, NH, MN)

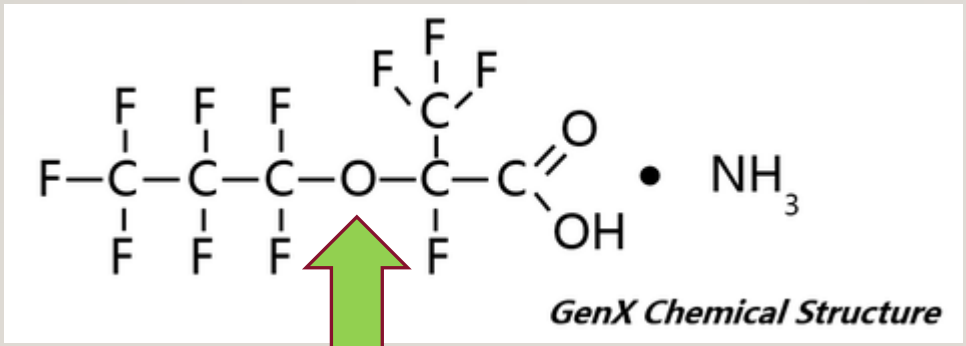
Thematic and not proportional.
Bottom of triangle indicates additional number of compounds; not a greater quantity by mass, concentration, or frequency of detection.

Figure 3-1. Emerging awareness and emphasis on PFAS occurrence in the environment
(Source: J. Hale, Kleinfelder, used with permission)

REPLACEMENTS FOR PFOA AND PFOS

- GenX (HFPO dimer acid) and ADONA
  - Perfluoroethercarboxylic acids used as fluoropolymer processing aids
- Shorter chain alternatives such as PFHxA (6 perfluorinated carbons) and PFBS (4 perfluorinated carbons)
- Are these safer?

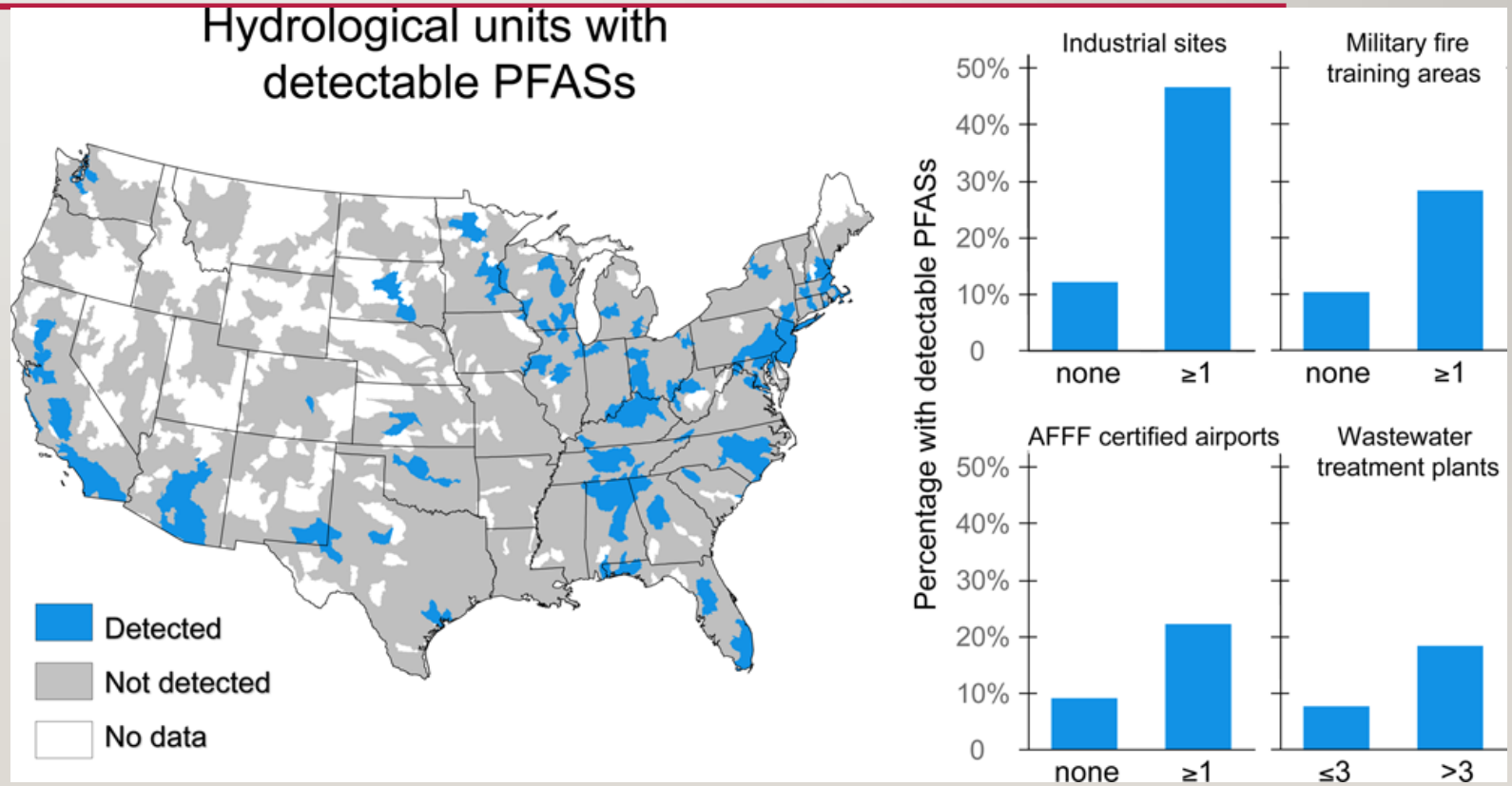




GenX Chemical Structure

PFAS IN PUBLIC WATER SYSTEMS

- 3rd round of Unregulated Contaminant Monitoring Rule (UCMR) sampling of public water systems included 6 PFAS and was conducted between 2013-2015
  - Showed where these PFAS have impacted large public water systems (>10K served) and some smaller systems



https://pubs.acs.org/doi/pdf/10.1021/acs.estlett.6b00260

PFAS HEALTH EFFECTS

- PFOA Cancer risk
  - Kidney, testicular (humans)
  - Testicular, pancreatic, and liver (animals)
- PFOS
  - liver tumors in animals.
- PFOA and PFOS exposures in humans over certain levels may result in adverse health effects, including:
  - changes in cholesterol,
  - developmental effects to fetuses during pregnancy or to breastfed infants (e.g., low birth weight),
  - liver effects (e.g., tissue damage),
  - immune effects (e.g., depressed antibody production in response to vaccination), and
  - thyroid effects.
- PFAS bind to proteins, phospholipids mimicry (K_{ow} not a good surrogate for bioaccumulation estimations)

AQUEOUS FILM FORMING FOAM (AFFF)

- 3 characteristics needed to meet fire fighting requirements for hydrocarbon fuel fires (such as Military Specifications)
  - "Aqueous" – water cools the temperature down
  - "Foam" – foam blanket blocks oxygen from the surface of the fire
  - "Film Forming" – film also forms on the surface of the hydrocarbon fuel to prevent vapors and any subsequent re-ignition
- An example of the hydrophobic and lipophobic PFAS properties
  - PFAS addition to aqueous phase allows the AFFF to quickly spread over the surface of the burning hydrocarbon fuel

https://dyayan.com/en/fire-fighting-foams_20

https://www.nist.gov/sites/default/files/documents/el/fire_research/R0201327.pdf

PFAS AT DOD SITES

- Historical use of AFFF in fire fighting training exercises and responses have resulted in PFAS contamination at many DOD sites
- After the UCMR3 sampling, DOD tested all 524 on-installation drinking water systems
  - 24 had PFOA/PFOS levels above 70 ppt (individually or combined)
  - Additionally, 12 systems where DOD was not the supplier had PFOA/PFOS levels above 70 ppt
- DOD has tested 2,445 off-base public and private drinking water systems
  - 564 of these had PFOA/PFOS levels above 70 ppt
- DOD identified and sampled 401 active and BRAC installations with known/suspected releases of PFOA/PFOS
  - 90 of these had PFOA/PFOS levels above 70 ppt
    - 2,668 groundwater wells sampled in this effort, with 1,621 wells above 70 ppt
- The National Defense Authorization Act was signed in December 2017 and authorizes a 5-year study to be conducted by CDC on PFAS health effects ($7M) and also $72M for Air Force and Navy to address PFAS contamination (Update: in most recent budget bill increased to $10M and $86M, respectively)

http://www.oea.gov/resource/addressing-perfluorooctane-sulfonate-pfos-and-perfluorooctanoic-acid-pfoa

WHERE CAN WE EXPECT PFAS TO BE FOUND?

- Fire fighting foam
  - There are 535 FAA 14 CFR Part 139 Airports
  - Railyards and oil refineries
  - Often a mix of PFAS in the foams, for example not just PFOS
- Metal plating and finishing
  - Dust suppression, wetting agents, and surfactant use of PFAS
  - Copper, Nickel, and Tin, as well as levelling agent for Zinc electrodepostion
- Waste Water Treatment Plants

WHERE CAN WE EXPECT PFAS TO BE FOUND?

- Landfills
- Textiles
  - Fabrics for jackets, shoes, umbrellas, tents
  - Carpets, upholstery, leather
  - Brand names Scotchgard (3M) and DuPont's Zonyl, Foraperle, and Capstone
- Paper and Cardboard Packaging
  - Plates, popcorn bags, pizza boxes, fast food wrappers, oven-safe papers (muffin cups/parchment paper)
  - Many of the PFAS used in food packaging have a phosphate functional group

WHERE CAN WE EXPECT PFAS TO BE FOUND?

- Industrial and Household cleaning products
  - Carpet/upholstery spot cleaners, denture cleaners, dishwashing liquids, floor polish, car wash products and waxes, wiper fluids, cleaners for wood, glass, countertops, and flooring
- Surface coating, paint, varnish, inks
  - Ink jet printer inks, ski waxes
- Plastics, resins, and rubber
  - Manufacture of PTFE and PVDF

WHERE CAN WE EXPECT PFAS TO BE FOUND?

- Adhesives
- Antifogging
- Cement Additives
- Oil Industry (surfactants in recovery wells)
- Mining Industry
- Photographic Industry
- Electronics Industry
  - Digital cameras, cell phones, printers, scanners, cable and wire insulation, fuel cell membranes (Nafion)

WHERE CAN WE EXPECT PFAS TO BE FOUND?

- Semiconductor Industry
- Etching
- Cosmetic and personal care products
  - Cosmetics, hair creams, toothpaste, dental floss
- Pesticides
- Medical Uses
- Oil Spills
- Solar panels

PFAS SAMPLING CONSIDERATIONS

- Sampling personnel/apparel:
  - Cosmetics, lotions, moisturizers
  - Sunscreens and inspect repellents (certain brands are ok)
  - Clothing washed in fabric softeners
  - Waterproof, water-resistant, stain-resistant clothing and boots (no Gore-Tex ®)
  - Coated Tyvek® suits
  - Fast Food Wrappers
- Sampling equipment:
  - Fluoropolymer bailers, pump bladders, tubing, valves
  - LPDE HydraSleeves
  - Waterproof field books
  - Sharpies
  - Post-it notes
  - Blue (chemical) ice
  - Aluminum foil

http://www.newmoa.org/events/docs/228/PFAS_Sampling_Chiang_Aug2016.pdf

FEDERAL PFAS REGULATIONS

- TSCA – Significant New Use Rules (SNUR) limit use of new chemicals that may pose risk to human health or the environment
  - 278 PFAS under SNURs
  - Section 5e orders can be issued when there is not enough information for EPA to make a determination on health or environmental effects
    - Requires facilities to restrict releases to air, water and land, protect worker exposures, perform toxicity and environmental fate testing, etc.

ONCE THE CONTAMINATION IS OUT THERE….

- Safe Drinking Water Act (SDWA) – can require action if "a contaminant present in or likely to enter a public water system or an underground source of drinking water… may present an imminent and substantial endangerment to the health of persons…"
  - Office of Water Health Advisory for PFOA and PFOS is now 70 ppt, individually or in sum
- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) – PFAS are not listed hazardous substances but may be addressed as CERCLA pollutants or contaminants, and investigations can include PFAS on a site-specific basis
  - RSL values for PFBS

ONCE THE CONTAMINATION IS OUT THERE….

- Clean Water Act? RCRA? Clean Air Act?
- RCRA 7002 orders have been filed to address PFAS contamination as "solid waste" that "may present an imminent and substantial endangerment"
  - Solid waste can be "any discarded material"
  - "*may* present endangerment"
  - RCRA 7002 lawsuits have been filed in AL, NC, and MI

DUPONT WASHINGTON WORKS – WEST VIRGINIA

- EPA issued combined TSCA and RCRA (3008) order, which settled in December 2005 for $16,500,000 (penalty and SEP combined)
- EPA Regions 3 and 5 issued SDWA 1431 order in 2002 (amended in 2006, 2009, and 2017) for PFOA impacts to groundwater used both in public water supply systems and private wells
- On January 11, 2018, EPA Region 3 issued a letter to Chemours requesting GenX sampling due to concerns about its use at the facility as a replacement chemical for PFOA, citing contamination issues at the Chemours Fayetteville Works site in North Carolina.

WOLVERINE WORLDWIDE - MICHIGAN

- Leather tannery with waste disposal issues (sludges/land application and landfilling)
  - 3M Scotchgard used to waterproof shoe leather
- Private wells impacted as high as 38,000 ppt (PFOA + PFOS)
- Extremely high total PFAS blood levels
  - Adult citizen, living adjacent to unlined landfill with 5,000 ppb PFAS blood level
  - Toddler using contaminated well has 484 ppb PFAS
- State of MI filed a 7002 order under RCRA on January 10, 2018
- EPA filed a CERCLA 106 removal order for metals on January 10, 2018

SAINT GOBAIN PERFORMANCE PLASTICS – NEW YORK

- Facility manufactured extruded tapes, circuit board laminates and PTFE coated fiberglass dating back to the1960's
- Saint-Gobain purchased the Site in1999 to manufacture a variety of polymer-based products that utilized PFOA, including high-performance polymeric films and membranes, as well as foams for bonding, sealing, acoustical and vibrational damping, and thermal management
- Site contaminants (in addition to PFOA) – TCE, VC, and PCBs
- Site was added to state SF list in January 2016 and the state requested that EPA add it to the NPL, which occurred on July 31, 2017

WHAT IS EPA DOING?

- EPA formed a cross-agency workgroup to address PFAS (December 2017)
- EPA is hosting a National Leadership Summit on May 22-23, 2018
- Following the summit, EPA will travel to states with communities impacted by PFAS
- EPA PFAS Website will be updated to include clearinghouse of PFAS information
  - https://www.epa.gov/pfas
- EPA PFAS Management Plan will be released later this year

EPA ACTIONS – PFAS EXPOSURE AND OCCURENCE

- Released EPA's Drinking Water Health Advisories for PFOS/PFOA
- Developed a laboratory method for measuring PFOS, PFOA and 12 other PFAS in drinking water (EPA Method 537)
- Creating two standardized analytical methods to quantify 24 PFAS analytes
  - Direct injection method for groundwater, surface water, and wastewater –method validation underway
  - Soil/sediment/solids method validation will begin Fall 2018
- Analytical method development for short-chained PFAS in drinking water is underway – external validation in early 2019
- Conducted monitoring for PFAS in drinking water under the third Unregulated Contaminant Monitoring Rule
- Currently assessing monitoring data from drinking water systems, along with health effects information, to make a regulatory determination on whether to initiate the process to develop a national primary drinking water regulation

EPA ACTIONS – HUMAN HEALTH IMPACTS

- Provided provisional Peer Reviewed Toxicity Values for PFBS for use in site decision making
- Identified the universe of PFAS currently being manufactured and used
- Collected scientific literature on toxicity
- Developing human health toxicity values for GenX and PFBS **(Summer 2018)**
- Providing states with access to test data obtained under TSCA authority for GenX chemicals (acid and salt) **(May 2018)**
  - Public comment period closed May 11 for EPA draft guidance regarding access to TSCA CBI materials

EPA ACTIONS – REDUCING PFAS EXPOSURES

- Created a PFOA Stewardship Program with industry to phase out manufacturing of PFOA
- Outlined drinking water treatment processes for PFOA/PFOS in drinking water
- Continuing site-specific technical assistance to identify and reduce PFAS exposures
- Updating EPA Drinking Water Treatability Database for multiple PFAS **(July 2018)**
- Will provide a description of federal authorities applicable to PFAS contamination **(May 2018)**
- Develop groundwater cleanup recommendations for PFOA/PFOS **(Sept 2018)**

EPA ACTIONS – STAKEHOLDER SUPPORT

- Ongoing robust public engagement effort with states, tribes, local communities, utilities, industry and the public
- Created an EPA regional coordination network to help EPA to support states and tribes in addressing PFAS
- Support PFAS outreach, including development of a PFAS webinar series **(ongoing)** and risk communication materials **(April 2018)**

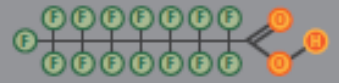
PFAS WHAT YOU NEED TO KNOW

WHAT ARE PFAS CHEMICALS?

Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that includes PFOA, PFOS and GenX chemicals. Since the 1940s, PFAS have been manufactured and used in a variety of industries around the globe, including in the United States. PFOA and PFOS have been the most extensively produced and studied of these chemicals. Both are very persistent in the environment and in the human body. Exposure to certain PFAS can lead to adverse human health effects.

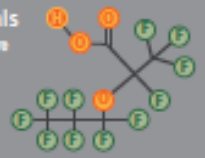
PFOA & PFOS

U.S. manufacturers voluntarily phased out PFOA and PFOS, two specific PFAS chemicals.



GenX Chemicals

GenX chemicals are a replacement for PFOA.



WHAT EPA IS DOING

Some of the agency's work includes: development of additional toxicity values, analytical methods for additional PFAS and non-drinking water media as well as treatment options for PFAS in drinking water. EPA is also hosting a National Leadership Summit on PFAS in May 2018.

Established methods to measure 14 PFAS compounds in drinking water

Identified five treatment processes for PFOA and PFOS

Identified all PFAS chemicals that are legally available for production and use

Provided national monitoring data for 6 PFAS in drinking water

Issued drinking water health advisories (70 parts per trillion) for PFOA and PFOS in 2016

Provided support for 10 states with site-specific PFAS challenges and problems: NC (Cape Fear River), MI, DE, WV, CO, NY (Hoosick Falls), OH, NH, VT and NJ

Updated website to include tools and information so that states, tribes and local communities can understand, assess and address PFAS incidents and emergencies

HOW ARE WE EXPOSED TO PFAS?

PFAS include a large number of important chemicals that can be used in some food packaging and can make things grease- and stain-resistant. They are also used in firefighting foams and in a wide range of manufacturing practices. Unfortunately, some of these substances don't break down over time. That means they build up in the environment and in our bodies.

Drinking water can be a source of exposure in communities where these chemicals have contaminated water supplies. Such contamination is typically localized and associated with a specific facility, for example,

- an industrial facility where PFAS were produced or used to manufacture other products, or
- locations where firefighting foam was used such as oil refineries, airfields or other training facilities for firefighters

If you are concerned about the possibility of PFAS in your drinking water, contact your local water supplier and ask for more information about PFAS.

STAIN/GREASE REPELLENT

FIREFIGHTING FOAMS

INDUSTRIAL USES

HEALTH EFFECTS

There is evidence that exposure to PFAS can lead to adverse health outcomes in humans. If humans or animals ingest PFAS (by eating or drinking food or water than contain PFAS), the PFAS are absorbed and can accumulate in the body. PFAS stay in the human body for long periods of time. In some cases, the level of PFAS in the body can increase to the point where people can suffer from adverse health effects.

Studies indicate that high concentrations of PFOA and PFOS can cause reproductive and developmental, liver and kidney, and immunological effects in laboratory animals. Both chemicals have caused tumors in animal studies. The most consistent findings from human studies are increased cholesterol levels among exposed populations, with more limited findings related to:

- infant birth weights
- adverse effects on the immune system
- cancer (for PFOA)
- thyroid hormone effects (for PFOS)

WWW.EPA.GOV/PFAS

SOURCE: U.S.EPA

CURRENT RESOURCES

- ITRC Fact sheets (six in total) https://pfas-1.itrcweb.org/fact-sheets/
  - Naming Conventions and Physical and Chemical Properties of PFAS
  - History and Use of PFAS
  - Regulations, Guidance, and Advisories for PFAS (very useful tables of current state regulations)
  - Environmental Fate and Transport
  - Site Characterization Tools, Sampling Techniques, and Laboratory Analytical Methods
  - Remediation Technologies and Methods
- CLU-In PFAS Webpage:
  - https://clu-in.org/contaminantfocus/default.focus/sec/Per_and_Polyfluoroalkyl_Substances_(PFASs)/cat/Overview/

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http://www.svfd.net/SVFD%20Files/Articles/Engineer/Foam%20Presentation%20web.pdf

Thanks to Linda Gaines with EPA OLEM, Office of Superfund Remediation and Technology Innovation